DEVELOPMENT OF A SEQUENTIAL TRACER GAS SAMPLER FOR USE IN UNDERGROUND COAL MINES

BY

J.-P. Farant, Ph.D, CIH
Wayne Wood, B.Sc, DOH
Steven Kibsey, B.Sc

Environmental Laboratories
School of Occupational Health
3450 University Street
Montreal, Quebec

WORK ON THIS PROJECT WAS CONDUCTED UNDER THE AUSPICES OF THE CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY, ENERGY, MINES AND RESOURCES, CANADA

MICROMEDIA
APR 23 1988

57 pp

DSS FILE NUMBER: 24ST.23440-4-9293
DSS CONTRACT SERIAL NUMBER: OST84-00409
CANMET PROJECT NUMBER:
CANMET SCIENTIFIC AUTHORITY: DR. A.W. STOKES

TABLE OF CONTENTS

	Page
INTRODUCTION	1
Literature Review	2
Study Objectives	8
METHODOLOGY	9
Preparation of CDE Charcoal Cloth	9
Standard Gas Generation	13
Preparation of Experimental Environment	14
CDE Charcoal Cloth Exposure	15
CDE Charcoal Cloth Analysis	
Thermal Desorption	16
Gas Chromatography	16
TEST PROTOCOLS	18
RESULTS AND DISCUSSION	21
CDE Charcoal Cloth SF_6 Adsorptivity Versus Time	21
CDE Charcoal Cloth SF_6 Adsorptivity Versus Tracer Gas Concentrations	25
SF_6 Adsorptivity of CDE Charcoal Cloth Versus Activated Nutshell Charcoal	35
CDE Charcoal Cloth Concomitant Exposure to SF_6 and Methane	35
Effect of Humidity on the Adsorption Capacity of CDE Charcoal Cloth	40

Page

Combined Effect of Methane Gas and Humidity on the SF_6 Adsorptivity of CDE Charcoal Cloth 45

Effects of Barometric Pressure on the Adsorptive Capacity of CDE Charcoal Cloth 46

Sample Integrity 47

CONCLUSIONS 48

RECOMMENDATIONS 51

REFERENCES 52

INTRODUCTION

The Environmental Laboratories, School of Occupational Health, McGill University has been contracted by CANMET, Department of Mines and Energy (contract 24ST.23440-49293) to determine the feasibility of designing a sequential sampler to monitor the tracer gas, sulfur hexafluoride (SF_6) in a coal mine environment.

A first phase of this investigation required the evaluation of a suitable adsorbent material for use with such a device. A charcoal cloth manufactured by the Charcoal Cloth Limited, Maidenhead, Berkshire, England namely, CDE Charcoal Cloth, was selected as a most likely material for this study. Tests conducted on the capacity of this cloth to adsorb, retain and quantitatively desorb SF_6 and the effect of coal mine environment conditions such as high relative humidity and methane gas on this capacity and its suitability to monitor tracer gas in a coal mine are reported herein.

Literature Review

Charcoal cloth was developed in 1972 [1] by Dr. F.A.P. Maggs at the British Ministry of Defence's Chemical Defence Establishment (CDE), Porton Down, Salisbury, Willshire, England as a highly efficient charcoal adsorbent material for chemical defence application.

In the Maggs' process, strong, flexible, activated carbon fibres are prepared by incorporating a Lewis acid, zinc chloride, into a fibrous carbohydrate namely, viscose rayon cloth, drying and flexing the cloth and carbonyzing it at 230°C for 15-25 minutes under nitrogen. Activation of the cloth is achieved by heating the material at 900°C for 15-25 minutes under CO_2, the activating gas [2].

The jet-black material generated does not disintegrate when handled. The cloth is pure charcoal and consists of a regular linen weave having thirteen double threads per centimeter. Each thread is in turn made up of many filaments having a diameter of 20 microns and whose individual strength approaches 400 kg/cm^2. The resulting cloth is flexible and both shock and vibration resistant. A summary of the cloth's physical properties are contained in Table I [3].

Charcoal cloth is rather unique among charcoal adsorbents in having a relatively smooth external surface coupled with a very high adsorptive capacity [4-6]. This superior adsorbency is due in part to its pore volume,

Table I. Physical Properties of CDE Charcoal Cloth [3]

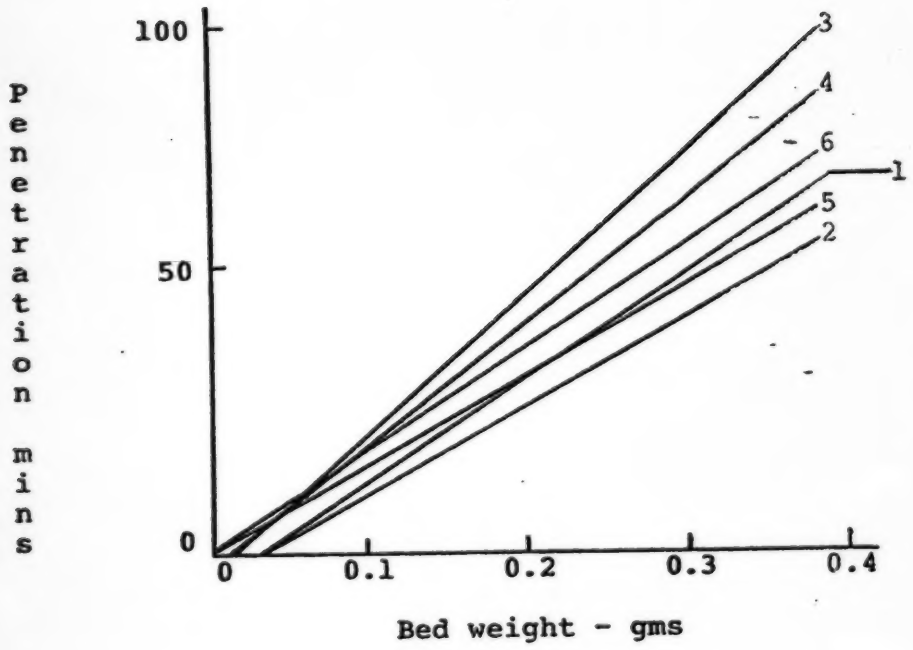
Physical Property*	Value
Surface density	9-16 mg/cm^2
Thickness	0.04-0.05 cm
Cross-sectional area	4×10^{-3} cm^2/cm
Breaking strength	2.5 - 3.5 kg/cm width
Tensile strength	$6.3 - 8.8 \times 10^5 gm/cm^2$
Flexirial rigidity	100-400 mg.cm (similar to dress linen)
Air flow resistance	pressure drop (P) across a number (n) of charcoal pads at linear air velocities (L cm/s) expressed as $P = KnL$ where $K = 11\text{-}18 \times 10^{-3}$ cm (water gauge)

* It should be noted that physical properties can vary with activation.

typically in excess of 0.6 cm^3/gm, pores whose diameters range from 0.4-2 nm, and its relatively fast absorption rate [7]. Values of the rate of adsorption for a wide range of gases and vapours are typically five to twenty times greater than that of other charcoal adsorbents such as nutshell charcoal [6]. Figure 1 exemplifies the striking difference in adsorptive capacity for a range of organic vapours.

Under ambient conditions all charcoals suffer some degradation in performance due to the presence of water vapour [8]. However, it has been demonstrated that this degradation is markedly less with charcoal cloth as shown in Figure 2 [6]. Thus, at a relative humidity of 80%, the performance of charcoal cloth is reportedly better than that of granulated nutshell charcoal by factors in excess of five. These differences in behavior have been attributed to different physical structures of the two materials and the difficulty of forcing out water from the micropores.

In 1977, Bailey et al. [9] of CDE, proposed a passive sampler which used CDE charcoal cloth for various organic vapours and gases. They reported that, for this cloth, steady state conditions are assured if the surface is exposed to gas or vapour partial pressures for times longer than 1-10 seconds (assuming a diffusion barrier <2.5μm). They also reported that the expected temperature dependence of the diffusion rate at ambient temperature levels would be less than 0.2% per ^oC. It is noteworthy that these workers were successful in using their prototype sampler to sample the gas



1 - Halothane 2 - Chloroform 3 - Carbon Tetrachloride

4 - Trichloroethylene 5 - Penthrane 6 - Chlorobenzene

Figure 1. Adsorptive Capacity of CDE Charcoal Cloth for Various Organic Vapours [6]

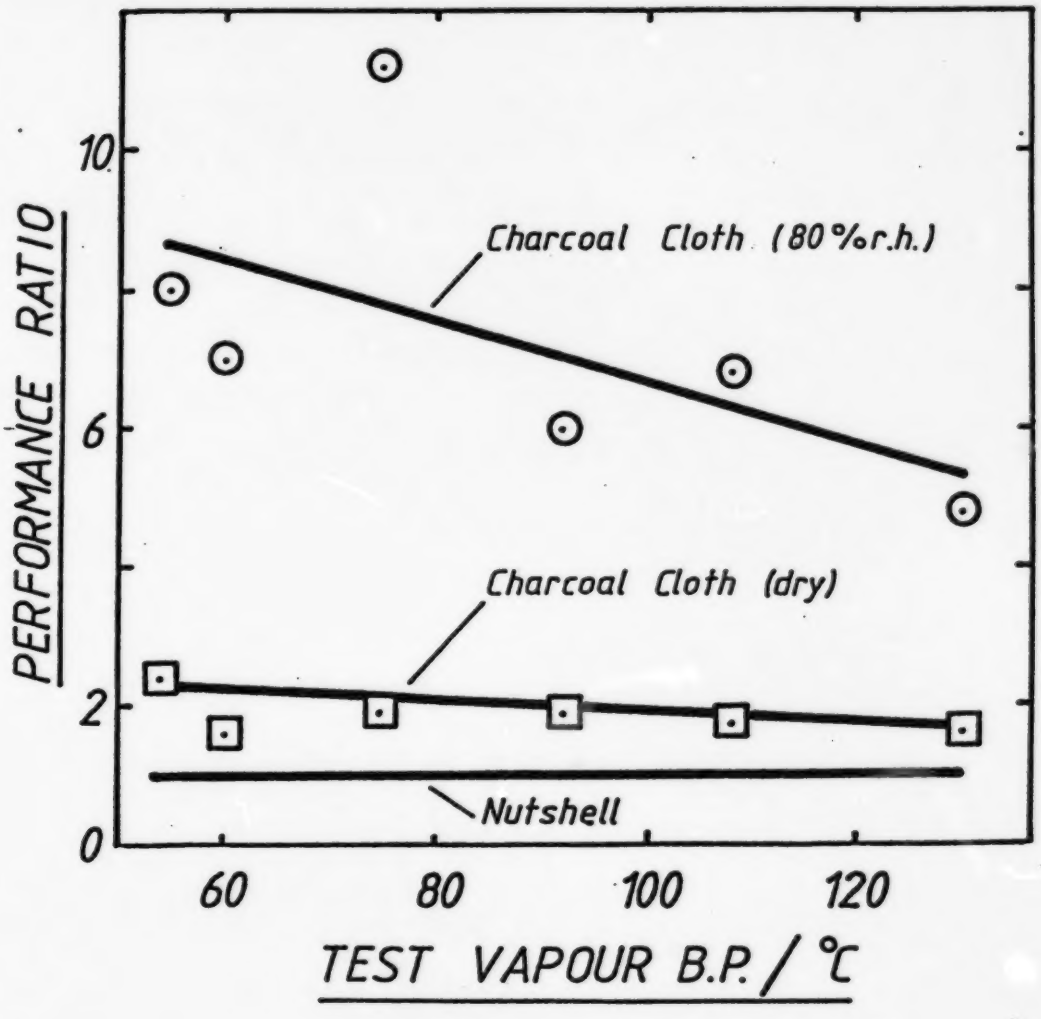


Figure 2. Performance Ratio for Various Organic Vapours - A Comparison of Charcoal Cloth and Nutshell Charcoal at High and Low Relative Humidity [6].

Freon-12 which was subsequently removed from the cloth by thermal desorption and analyzed with Wilks 20.3 path length cells and an infrared spectrophotometer.

Telephone conversations with Drs. Bailey and M.E. Smith, at CDE concerning their previous work with the CDE charcoal cloth revealed that no one at CDE had attempted to use a passive sampler incorporating this cloth to collect SF_6 samples. However, Koresh and Soffer [10-14] have extensively studied the passive adsorption of SF_6 on a similar carbon cloth called TCM 128, manufactured by Carbone-Lorraine, Paris, France. After oxidative activation this cloth was used for their investigation of stereospecificity in the adsorption of simple molecules with critical cross-o sectional diameter ranging from 3.6 to 5.6 A [10-14]. They have conclusively demonstrated in these studies that SF_6 is readily (passively) adsorbed on activated charcoal cloth. It should be mentioned that their parallel investigations of the adsorption of water vapour on such cloth have shown it to be related to the presence of surface oxides. Assuming that there are no significant differences between the two types of charcoal cloth, it could be expected that similar adsorptive results would be obtained with the CDE charcoal cloth.

To our knowledge, the foregoing literature review comprises most of the pertinent work performed to date on charcoal cloth and its ability to adsorb sulfur hexafluoride.

Study Objectives

As per the "Statement of Work, Appendix A", contract 24ST.23440-49293, this study will attempt to demonstrate that CDE charcoal cloth is a suitable material for a sequential sampler to be used to collect SF_6 in coal mines. That is, that CDE charcoal cloth can adsorb, retain and quantitatively thermally desorb SF_6 for analysis and is not unduly affected by methane and water vapour found in coal mine environments and changes in temperature and barometric pressure. Whenever applicable, the performance of charcoal cloth will be compared to that of comparable activated charcoal material.

METHODOLOGY

Preparation of CDE Charcoal Cloth

Initially, sections of the bolt of CDE charcoal cloth received from the charcoal cloth Ltd. (Maidenhead, Berkshire, England) were cut into strips approximately 4 x 1 cm in size and weighing 0.05 grams. Later and, for reasons to be discussed, 4 x 0.4 cm strips weighing 0.015 grams were prepared and placed inside brass mesh strips (37% open face area) 6 x 0.5 cm, .025 cm thickness, 150 mesh.

Both types of charcoal cloth samplers were placed inside individual thermal desorption (Perkin Elmer ATD50, Figure 3) sample tubes attached to a brass manifold (Figure 4.)* and heated at 350°C for 12-16 hours under a stream of nitrogen gas (Linde prepurified grade). This was accomplished by placing the manifold and attached nitrogen line inside a gas chromatograph oven, usually overnight. As an extra precaution the nitrogen gas was passed through three cartridges (Chromatographic Specialties models MT200-4, OT3-4 and HT200-4) to remove water, oxygen and hydrocarbons before it entered the manifold. A second method of cleaning and

* The manifold consists of a 30 cm long, 4 cm diameter hexagonal rod with a 1.2 cm hole bored down the center. There are 18 x 0.6 cm holes drilled perpendicularly into the center bore, each equipped with an N.P.T./Swagelock adaptor. The 18 ATD-50 tubes containing samples to be cleaned are connected to the adaptors using 0.6 cm graphite ferrules.

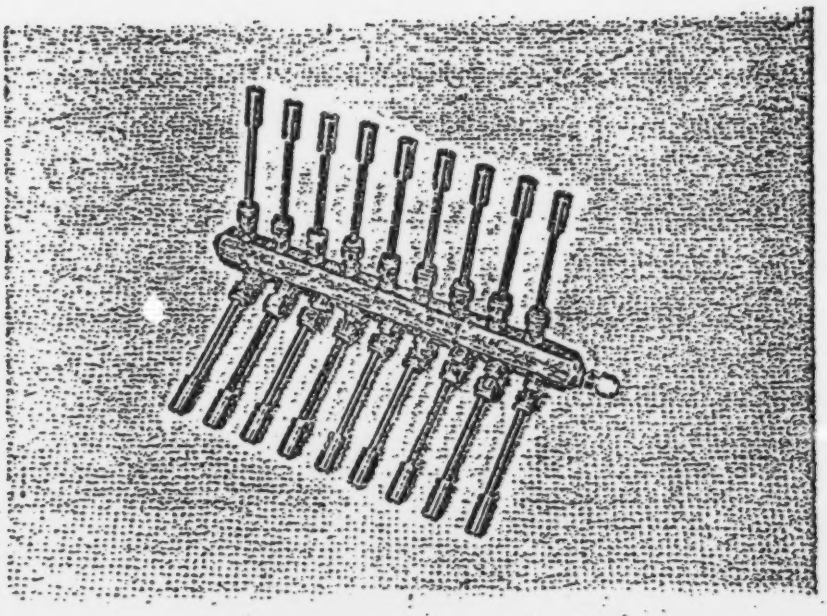


Figure 3. Brass Manifold

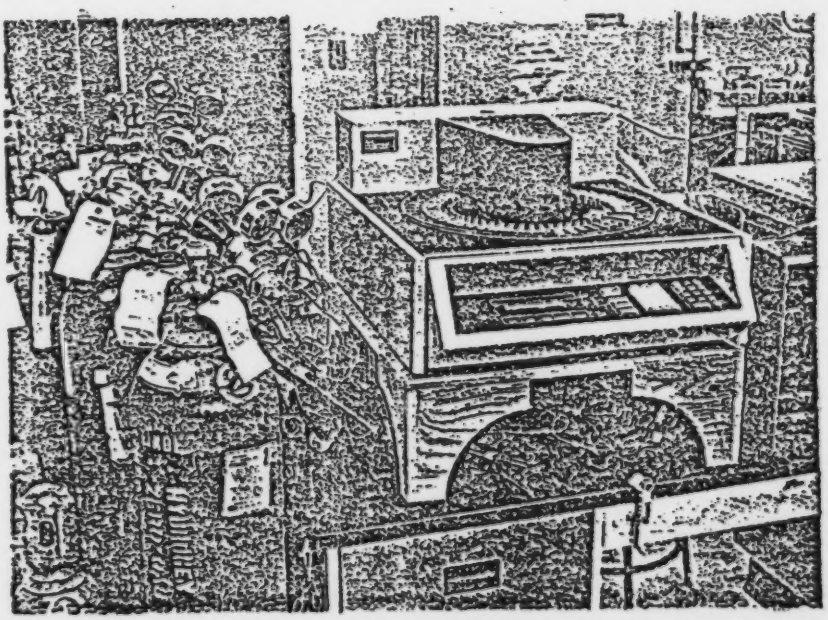


Figure 4. Perkin-Elmer ATD-50 Automatic Thermal Desorber

activating the cloth was used during more recent tests. This involved repeated thermal desorption of the samplers contained in their respective ATD-50 sample tubes over a period of several days. Although the method proved equally effective, it required more time.

The test samplers were checked for residual contamination by placing them in the ATD-50 and analysing their gaseous emissions under selected analytical conditions (details given later) with a Varian gas chromatograph (model 3700) equipped with an electron capture detector. Only samples showing minimal contamination were chosen. It is interesting to note, that test samplers, once cleaned and activated, require lower temperatures (250°C) and shorter reactivation periods under nitrogen gas (10 minutes).

For long-term storage (> 2 days), the cleaned and activated test samplers, still in their ATD-50 tubes, were sealed under nitrogen gas by capping the ATD-50 tube ends with parafilm. It is suspected that previous contamination of the stored samples was caused by emissions of volatile compounds by the O-rings of the ATD-50 tubes. The manufacturer of the ATD-50 instrument will provide silicone O-rings which will hopefully alleviate this problem.

Following pre-tests, the tubes containing the cloth samples were placed in the environmental chamber's (Figure 5) airlock prior to performing the SF_6 exposure tests.

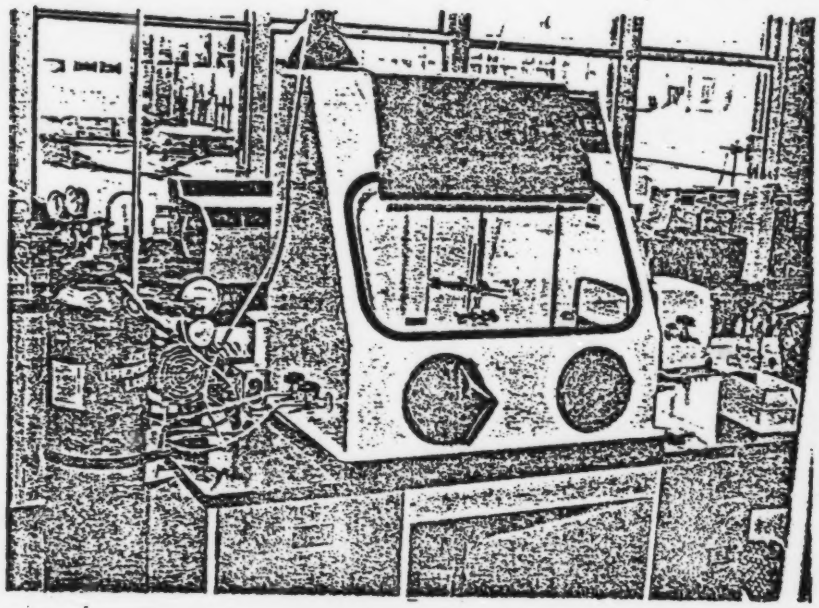


Figure 5. Environmental Chamber (LabConco)

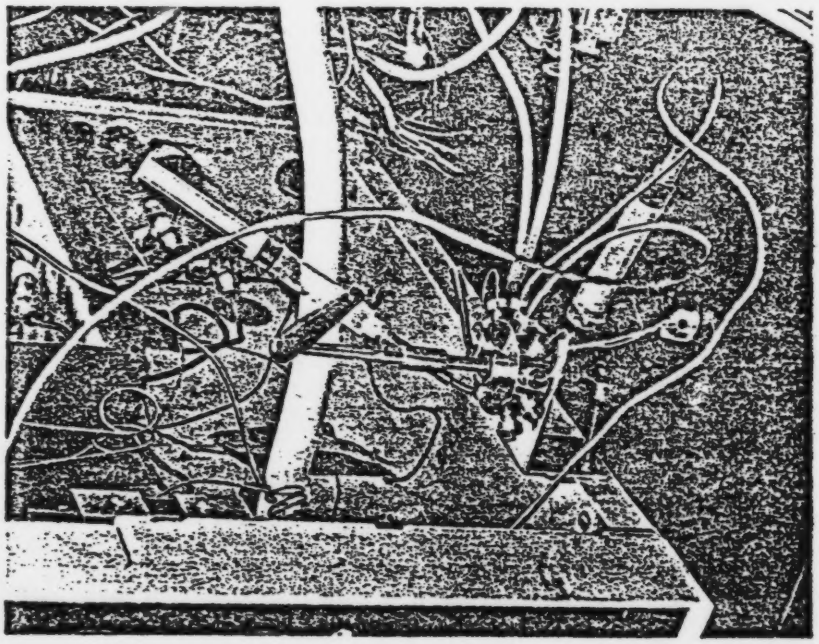


Figure 6. Automatic Sampling Valve

Standard gas generation

Standard concentrations of SF_6 were prepared for two reasons: to calibrate for the response of the instrument each day, and to fill the environmental chamber with the experimental mixtures. These were prepared with a VICI Metronics, Model 340-58-D Dynacalibrator and a SF_6 permeation device (VICI Model WD). Since the release rate of SF_6 is constant at a given temperature, controlling the dilution rate and monitoring it using a bubble meter allowed for accurate preparation of a wide range of standard concentrations.

During the first stage of the study, a 0.94% (in air) mixture of methane gas (Matheson, analysed, 0.94% CH_4 balance air) was used as the dilution for the SF_6 gas generator. Recently, higher concentrations of methane gas were tested, and this was achieved by introducing pure methane gas (Matheson commercial grade) into the chamber. The concentration of methane inside the chamber was then measured using a Biosystems model 100 Combustible Gas Meter which is portable enough to store inside the chamber itself. Continuous monitoring was accomplished by drawing air through the combustible gas monitor's cell using a portable sampling pump. The meter was calibrated daily using the 0.94% analyzed gas mixture.

Preparation of Experimental Environment

A Labconco controlled atmosphere chamber, Model 50004, (Figure 5) was used to conduct cloth exposure tests under a variety of environmental conditions. Prior to each test, the chamber was evacuated to 5" water guage pressure and the test gases, SF_6 from the standard gas generator and CH_4, from the compressed gas cylinger were introduced until a slight positive pressure was achieved, 0.5 H_2O up to 1.25 kilopascals above atmosphere. (The pressure limit of the chamber is 1.25 kilopascals above atmosphere). The concentration of the tracer gas was periodically verified before, during, and after the tests by introducing samples from the chamber into the gas chromatograph (Varian model 3700 equipped with a nickel-63 electron capture detector, later replaced with a Perkin-Elmer model 8310B). The methane concentration was determined using the combustible gas meter. Once the desired concentration was attained and equilibrium established (1-2 hours) all inlets and outlets to the chamber were closed. Leakage in the chamber was minimal, allowing for several experiments to be performed using the same standard gas preparation.

It was found that the SF_6 concentration could be increased in the chamber without diluting the CH_4 by introducing a permeation device (VICI model WD) into the chamber and removing it when the desired concentration was achieved. This method differed from introducing SF_6 from the standard generator in that it did not alter chamber pressure.

To perform tests in atmospheres of elevated humidity a Bionaire model 200 ultrasonic humidifier was kept inside the chamber. It facilitated generation of controlled humidities to as high as 95%. The relative humidity inside the chamber was verified using a Bendix motorized psychrometer.

CDE Charcoal Cloth Exposure

Prior to exposing the cloth, the desorber tube was pressurized by removing the end cap and introducing a stream of nitrogen. This was done to prevent re-entry of the chamber's environment. The nitrogen flow rate was kept low (<4 ml/min) to minimize dilution of the chamber's atmosphere. The other end of the tube was opened and the brass mesh containing the cloth sample or bare cloth sample was removed using tweezers and exposed for a measured amount of time. Following exposure the cloth was reinserted into the tube and purged for three more seconds to ensure that interstitially trapped chamber air is removed.

Following the exposure test, the samples were returned to the airlock until analysis.

CDE Charcoal Cloth Analysis

Thermal desorption

Within one hour of the experiment, the tubes containing the sampes were placed in the carousel of the Perkin-Elmer ATD-50 and thermally desorbed at the following conditions:

Oven Temperature: 250°C
Box (valve) Temperature: 70°C
Desorption Time: 4.0 min
Cold Trap Low Temperature: 20°C
Cold Trap High Temperature: 300°C
Analysis Time: 4.0 min
Total Cycle Time: 10.0 min

Gas Chromatography

The ATD-50 heated transfer line was connected directly to the column of a Varian model 3700 gas chromatograph equipped with a nickel-63 electron capture detector. The chromatograph was also equipped with a gas sampling valve fitted with a 25-microlitre injection loop (Figure 6). This permitted direct injection of SF_6 mixtures from the standard generator and from the environmental chamber. Detector response was monitored with a strip chart recorder and a reporting integrator (Hewlett-Packard 3390A) which provided simultaneous readout of two response ranges.

During the latter stage of the study, the Varian chromatograph was substituted with a Perkin-Elmer 8310B equipped with the same type of detector and gas sampling valve. The recording systems were replaced with a Perkin-Elmer LCI-100 Data Computing System. This configuration

provided automated control of the ATD-50 facilitating overnight analysis and reducing the amount of labour. However it was found that the PE 8310B detector saturated at a lower concentration of SF_6 (30 ppb) than the Varian 3700 (>117 ppb). For this reason, tests for humidity were run at SF_6 concentrations of 20 ppb and lower. This changeover in instruments requires a 3-week interruption in instrumentation.

Chromatographic analysis was performed under the following conditions with both instruments.

Column:	Molecular Sieves, 6' x 1/8" stainless steel
Carrier:	Prepurified grade nitrogen
Carrier flow:	30 ml/min
Column Temperature:	60°C
Detector Temp.:	250°C
Attenuation Range:	16-512

TEST PROTOCOLS

The adsorption of SF_6 on CDE activated charcoal cloth was measured as a function of time and ambient concentration, and tested in conditions simulating those of a coal mine environment namely elevated humidity, methane gas concentration and barometric pressure. A comparison of the adsorptive capacity of CDE charcoal cloth compared to that of activated granular nutshell charcoal was performed as well as some checks for sample integrity. Barometric pressure, relative humidity and ambient temperature were recorded throughout the test periods.

1) Time. Seventeen samples of CDE charcoal cloth were prepared, inserted in ATD-50 desorber tubes, exposed to a known concentration of SF_6 in the environmental chamber for measured periods of time, and analysed as previously described. Sampling times tested were 2, 5, 10, 15, 20, and 30 seconds. Each series of tests included two control samples: one unopened tube (to verify cleanliness of cloth) and one empty, opened tube (to determine that only the cloth is capturing SF_6). A limited number of short sampling times (<5 sec or less) were employed, since the manual nature of the procedure made them difficult to control.

2) SF_6 Concentration. The above test (1) was repeated at a number of different SF_6 concentrations, ranging to 117 ppb, each time ensuring that several exposure periods of

10 seconds were employed. This was the exposure time predominantly used in the effect of SF_6 concentration study.

3) Elevated Humidity. As soon as a series of tests was complete, at ambient humidity, the humidity in the chamber was raised. Thus, during the desorption and analysis period, the humidifier was activated, allowing establishment of steady-state conditions in time for the next tests. This provided comparison of two series of tests, identical in every respect except humidity. The sampling protocol was virtually the same as test (1) above.

4) Methane Concentration. To test the effects of methane gas on the adsorption of SF_6 on charcoal cloth, the CH_4 concentration was held between 2 and 4.5%. It was not possible to introduce methane into the chamber without altering the SF_6 concentration. However, it could be measured accurately. It was therefore necessary to create a new chamber environment for each series of tests on the effects of methane. Increases in CH_4 concentrations could be made only by introducing pure CH_4 into the chamber; decreases could be achieved by purging. Therefore, test conditions for effects of methane may vary slightly from those for effects of other parameters. The testing protocol was the same as that for test (1) above.

5) Performance Comparison to Granular charcoal. The ability of CDE activated charcoal to passively adsorb SF_6 was compared to the ability of activated granular nutshell charcoal to actively adsorb SF_6. ATD-50 tubes were packed with 500 mg of activated charcoal granules and heated to 250°C under nitrogen gas overnight to clean them. They were checked for acceptability in the ATD-50 by the same manner as described previously for the cloth. Tubes were individually connected to a MDA low flow pump and samples were collected at .21cc/sec for 10, 20, and 30 seconds from varying concentrations of SF_6 in air. The test samples were analysed as described previously and the results compared to those obtained with CDE charcoal cloth in earlier experiments. For these tests, the cloth was not wrapped with brass mesh.

6) Sample Integrity. In separate tests, ten other samples of CDE charcoal cloth were prepared and exposed to a known concentration of ambient SF_6 for 10 seconds and 20 seconds. Five samples were analysed immediately and the remaining five samples were allowed to stand at room temperature for 24 hours before being analysed.

7) Sample Consistency. To determine the amount of variation in the prepared samples, a series of tests was performed using the same tube over a range of SF_6 concentrations. Results were compared to those using a variety of tubes.

RESULTS AND DISCUSSION

CDE Charcoal Cloth SF_6 Adsorptivity Versus Time

The goal of this project is the design of a sequential sulfur hexafluoride sampler for use in a coal mine which has the capability of collecting sufficient tracer gas for analysis after a 10-second sampling period or less. Preliminary tests performed with 4 X 1 cm bare cloth test samples at SF_6 concentrations <10ppb and for a 10-second exposure time demonstrated conclusively that the CDE cloth could meet this requirement. This fact is clearly illustrated in Figure 7. The results of the SF_6 gas chromatographic analysis of the exposure chamber atmosphere (300 ppt SF_6) are compared to that of the thermal desorption of a test cloth sample exposed to this atmosphere for 10 seconds. Unfortunately, these results also indicated that the test cloth samplers used could not be exposed to concentrations of SF_6 exceeding 2-5 ppb for periods >10 seconds. The amount of tracer gas released during thermal desorption saturated the output of the gas chromatograph's electron capture detector. The results of inital exposure tests (Figure 8) conducted with these bare cloth samplers at tracer gas concentrations ranging from 0.3 to 1.5 ppb and for a 10-second exposure period attest to this serious limitation. No efforts were made at that time to determine the adsorption pattern for SF_6 at times <10 seconds. The extrapolation shown in Figure 8 may therefore not reflect the actual situation. It is noteworthy that follow-up thermal

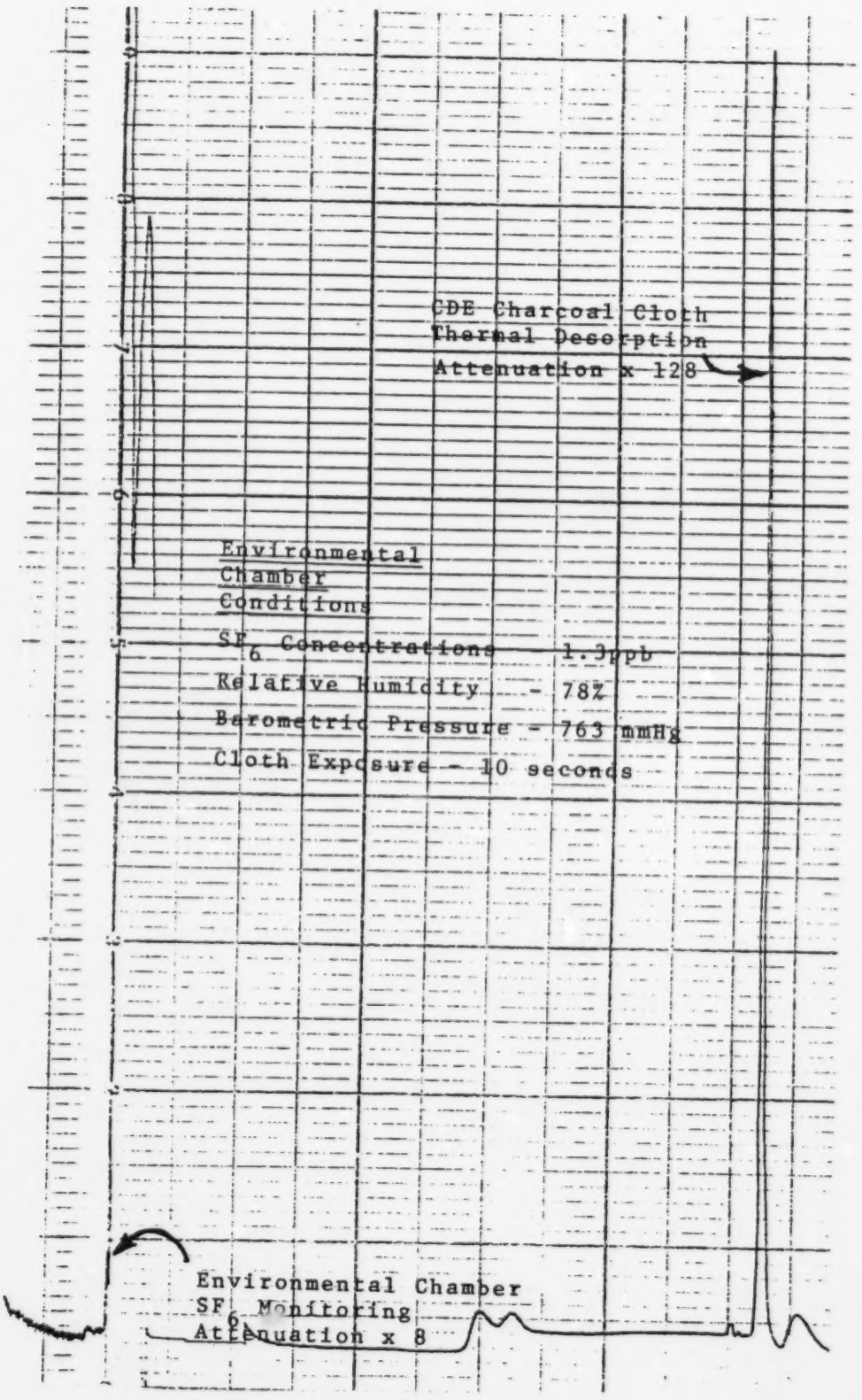


Figure 7. Gas Chromatograms of Chamber Concentrations and CDE Cloth Thermal Desorption

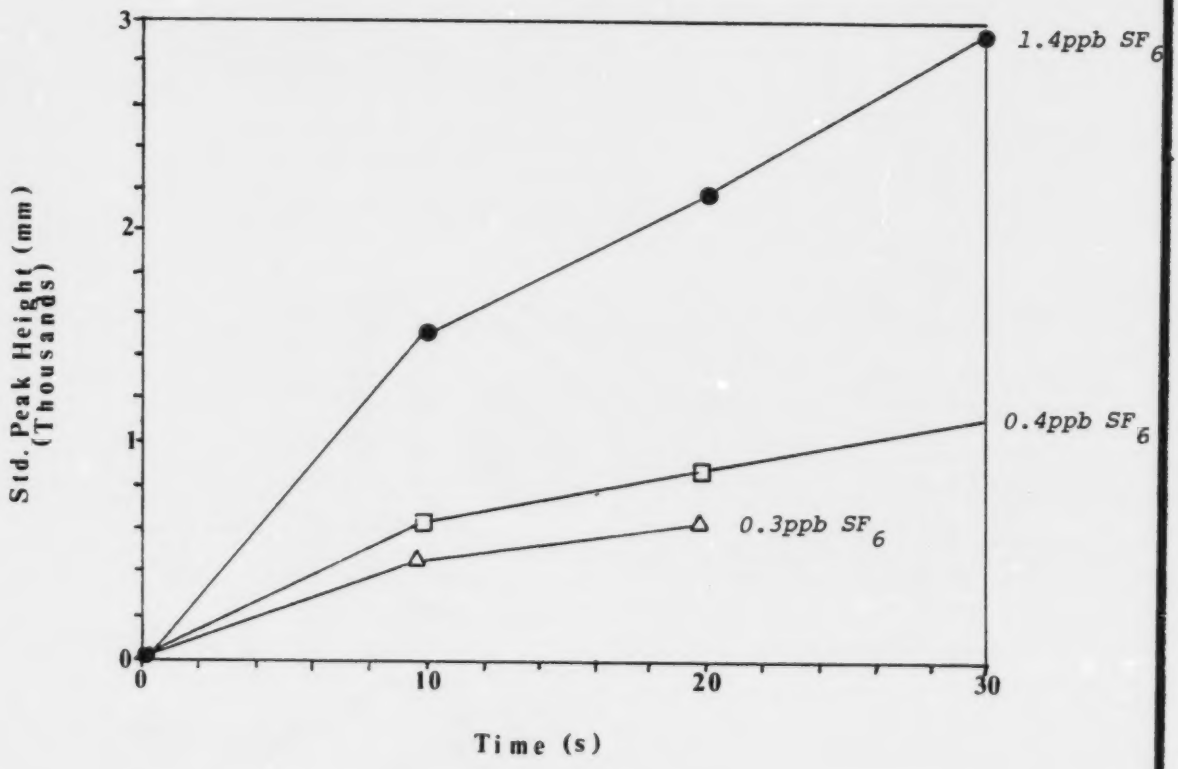


FIGURE 8: PEAK HEIGHTS RECORDED AFTER THE THERMAL DESORPTION OF CDE CHARCOAL CLOTH SAMPLES EXPOSED TO VARIOUS CONCENTRATIONS OF SF_6 AT DIFFERENT EXPOSURE TIMES.

CANMET 24ST. 23440-49293		
FIG: 8	19/07/85	

desorption of the test cloth samplers used showed no residual SF_6, indicating quantitative desorption of the gas.

According to the relationship which determines the amount of SF_6 adsorbed by the cloth namely,

$$M = \frac{DA}{L} \text{ c.t.}$$

where, M = mass of SF_6 adsorbed c = SF_6 concentration

D = diffusion coefficient (constant) t = time of exposure

L = diffusion path length

only two variables can be manipulated to reduce the amount of tracer gas adsorbed at a certain concentration and time of exposure: diffusion path length (L) and the cloth's surface area(A). Modifications were therefore performed on the cloth sampler to expand the test range of SF_6 concentrations. The size of the cloth sample was reduced to 4 x 0.4 cm, a 60% reduction of the area. The cloth was then wrapped with a fine brass mesh whose open face area was 37% thereby reducing the exposed cloth area a further 3%. This alteration also introduced a diffusion path length of .025 cm. The brass also provided better protection for the cloth, preventing it from becoming frayed during handling. The latter modification was also made in an effort to minimize the anticipated isokinetic effects at the cloth's face. The brass mesh/cloth sampler was used for the balance of the investigation reported here.

The modified samplers were exposed to SF_6 concentration

ranging from 7-117 ppb for 2, 5, 10, 20, 30 and 60 second periods. The results of one of these studies are shown in Table II along with ambient humidity. Ambient temperature ranged from 22-25^{o}C and barometric pressure was normal during these tests. All results show a marked increase of SF_6 adsorbed with time of exposure. However, at exposure times > 20 seconds, the results are somewhat erratic (Figure 9). The relationship between the amount of tracer gas adsorbed and ambient SF_6 concentrations is also markedly curvilinear at all concentrations. This occurrence could be attributed to an isokinetic effect at the face of the cloth sampler. A comparison of the results from Figures 8 and 9 shows that the brass mesh protecting the cloth has had little apparent effect on this or other parameters responsible for the curvilinearity.

CDE Charcoal Cloth SF_6 Adsorptivity Versus Tracer Gas Concentrations

Preliminary tests of adsorption of SF_6 on a bare charcoal cloth at a fixed sampling time, 10 seconds, and at different ambient concentrations of SF_6 gave the results depicted in Figure 10. The graph confirms the serious limitations of this type of sampler discussed earlier and show a curvilinear response at relatively low SF_6 concentrations. The results of representative tests performed with the brass mesh/cloth samplers exposed to SF_6 concentrations ranging from 7-117 ppb and for fixed sampling

TABLE II. CDE CHARCOAL CLOTH EXPOSURE TO VARIOUS CONCENTRATIONS OF SF_6 (ppb) FOR DIFFERENT PERIODS (seconds)

SF_6 CONCENTRATION (ppb)	RELATIVE HUMIDITY (%)	GAS CHROMATOGRAPHIC RESPONSE (mm) AFTER VARIOUS EXPOSURE PERIODS (seconds)					
		2	5	10	20	30	60
7	48.5	(1)* 472	(2) 476 ± 39	(3) 821 ± 115	(1) 872	(1) 744	(1) 600
22	35.5		(1)2240	(2)2357 ± 294	(2)2800 ± 339	(2)2928 ± 339	
40	44.5		(2)3649 ± 271	(3)3019 ± 532	(2)3600 ± 68	(2)4080 ± 566	
43	54.0	(2) 2912 ± 679	(1)2592	(4)3989 ± 665	(2)4560 ± 701	(2)3920 ± 792	
48	37.5		(2)3904 ± 1493	(2)2928 ± 475	(1)4448	(2)4304 ± 701	
56	58.8	(2)3456 ± 543	(2)3264 ± 362	(3)5281 ± 500	(1)5728	(2)5008 ± 611	(1)3360
83	56.0		(2)4128 ± 181	(3)4405 ± 551			
85	53.0	(2)3408 ± 1018	(1)3328	(3)4490 ± 702	(2)4690 ± 769	(2)3136 ± 1221	(1)3776
117	53.0		(1)6400	(3)5611 + 480	(2)6688 ± 407	(2)7008 ± 498	

* Number of test samples.

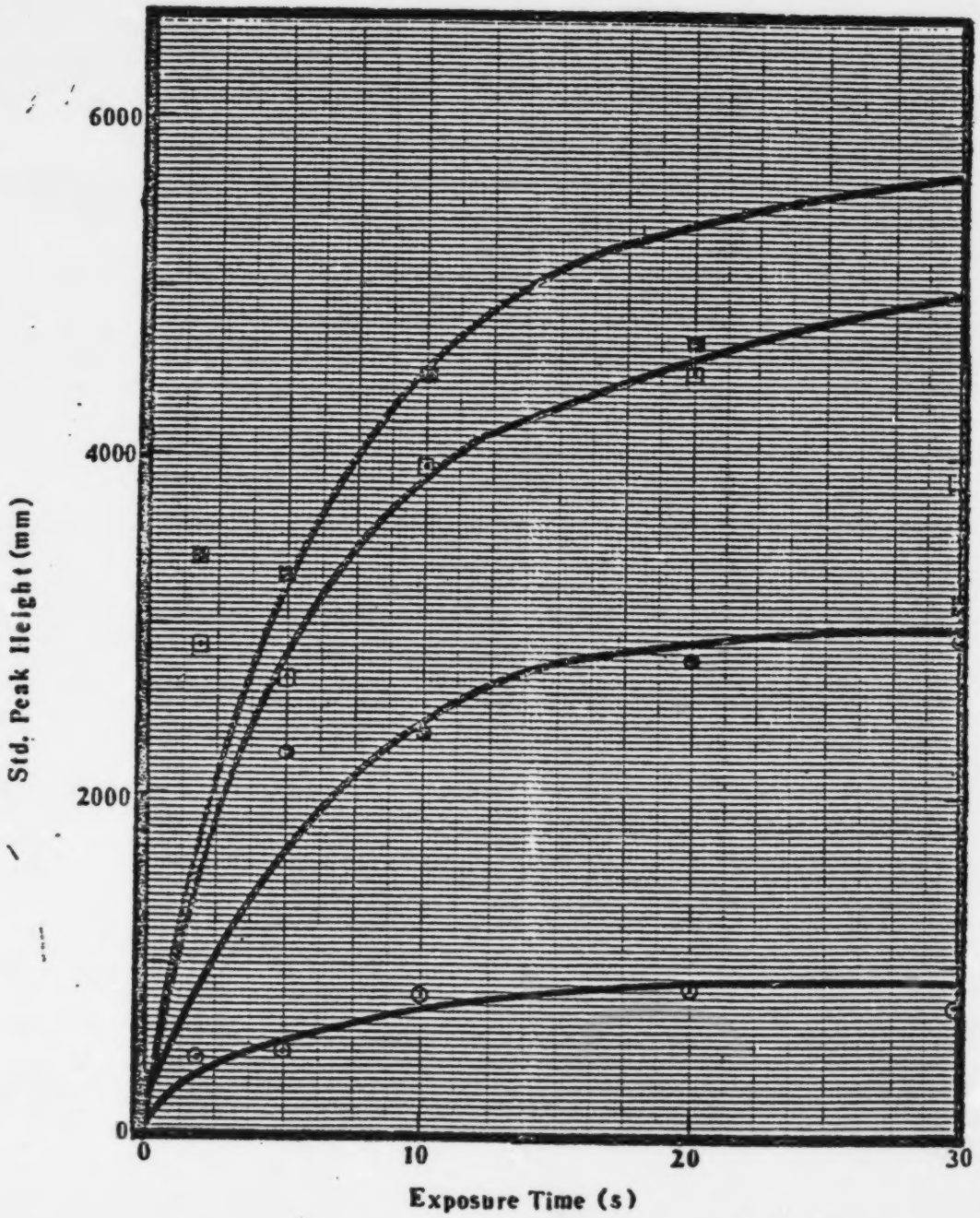


FIGURE 9: PEAK HEIGHTS RECORDED AFTER THE THERMAL DESORPTION OF BRASS MESH/CLOTH SAMPLER EXPOSURE TO VARIOUS CONCENTRATIONS OF SF_6 FOR DIFFERENT SAMPLING PERIODS.

CANMET 24ST.23440-49293		
FIG: 9	19/07/85	SK

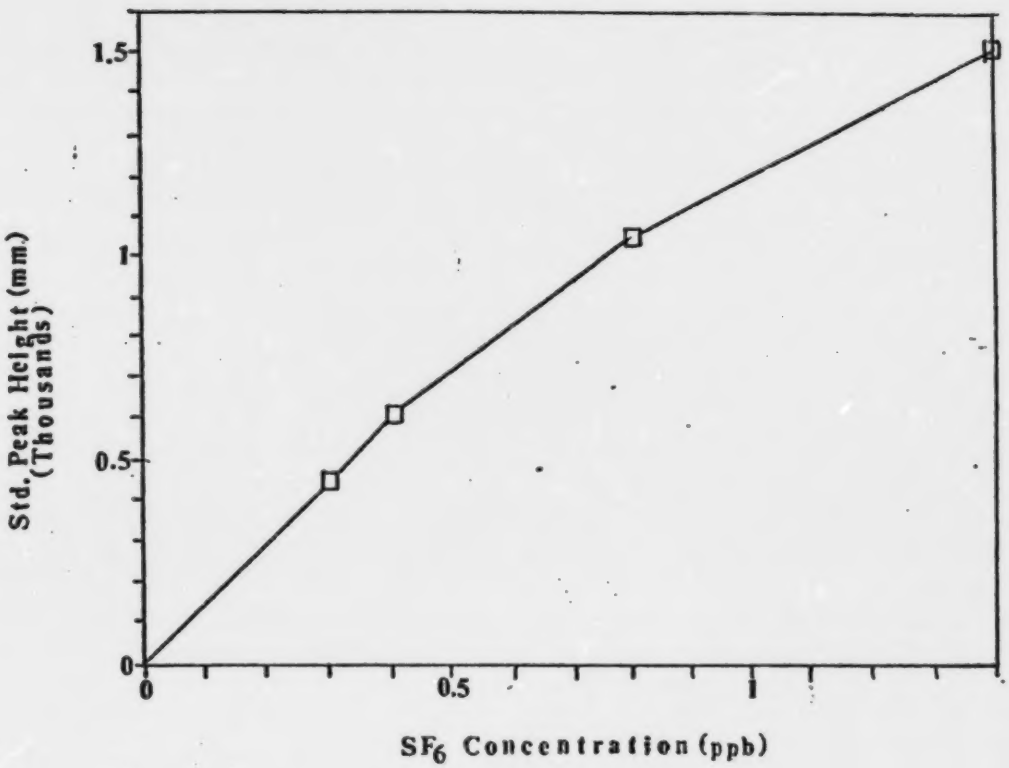


FIGURE 10: ADSORPTION OF SF_6 BY CDE CHARCOAL CLOTH AT VARIOUS CONCENTRATIONS OVER A 10-SECOND PERIOD.

CANMET 24ST. 23440-49293		
FIG:10	19 /07/ 85	

periods of 2, 5, 10, 15, 30, and 60 seconds are given in Table II and shown in Figures 11-14. In this instance, results obtained from tests performed at exposure times <10 seconds show greater variability. This variability could be attributed to difficulty in reproducing exposure times at the 2 and 5 second periods. The 10-second period results, although still displaying some irregularities, was selected for future tests since this sampling period met one of the requirements for the sequential sampler, it was more reproducible and was not apparently subject to the factor(s) affecting adsorption at larger sampling times. It is notable that the average coefficient of variation (C_V) for the 10-second sampling period was an acceptable 0.13.

The relationship between the amount of SF_6 adsorbed on the cloth and the concentration of SF_6 in the test chamber atmosphere is curvilinear (Figures 11-14). A plot of the log of SF_6 concentration versus detector response for the 10-second sampling period yields a linear relationship (r= 0.91, y= 6.6, Figure 15). The observed curvilinearity of the relationship could be attributed to an isokinetic effect.

The CDE cloth's SF_6 saturation point has not been estimated. Based on the results presented here and on previous reports [10-14], this saturation should occur at relatively high concentrations (>120 ppb).

Recent tests conducted at the selected 10-second sampling period have revealed one important source of

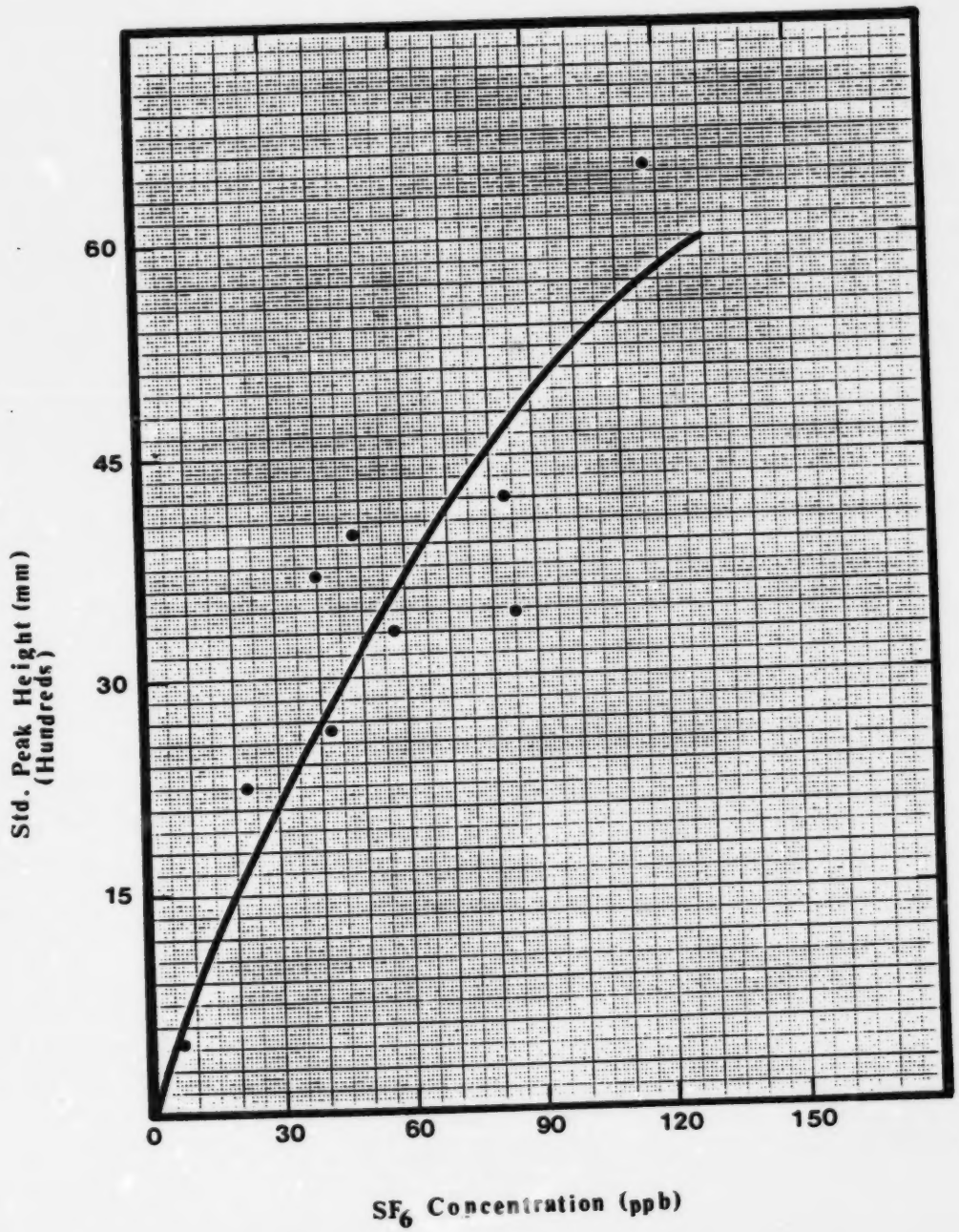


FIGURE 11: PEAK HEIGHTS RECORDED AS A FUNCTION OF SF_6 CONCENTRATION - 5 SECOND PERIOD.

CANMET 24ST. 23440-49293		
FIG: 11	19/07/85	

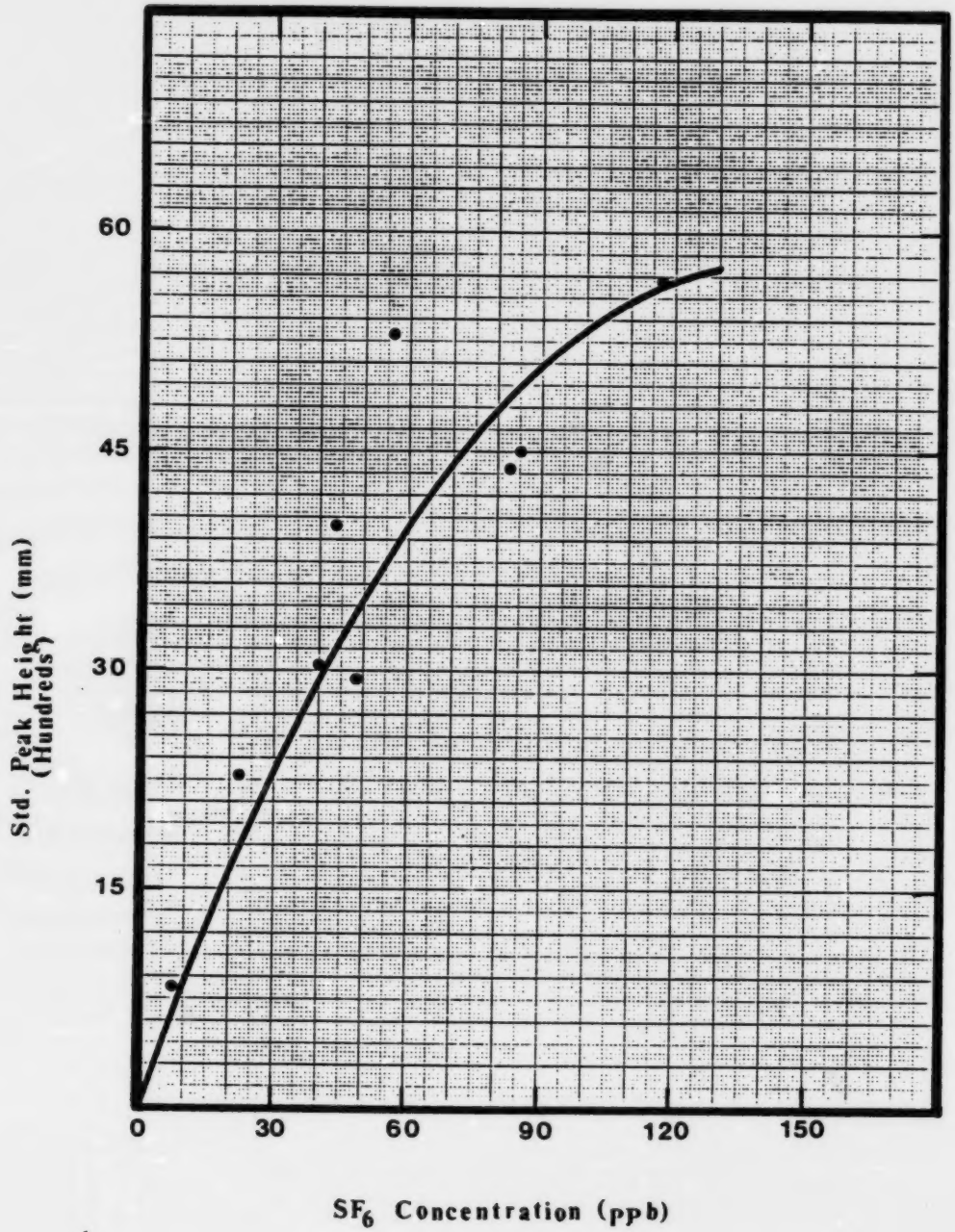


FIGURE 12: PEAK HEIGHT RECORDED AS A FUNCTION OF SF_6 CONCENTRATION - 10 SECOND EXPOSURE PERIOD.

CANMET 24ST. 23440-49293		
FIG:12	19/07/85	

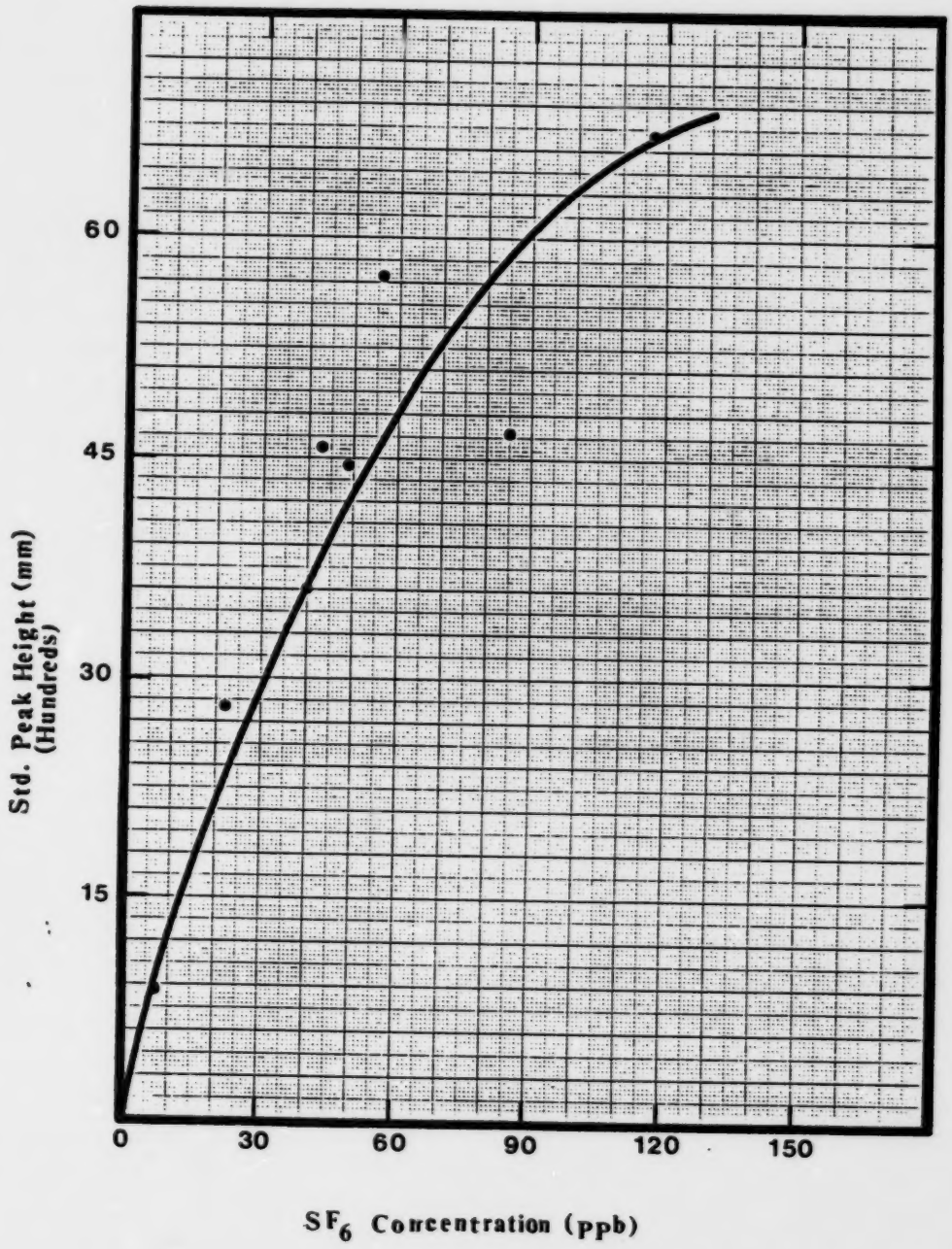


FIGURE 13: PEAK HEIGHT RECORDED AS A FUNCTION OF SF_6 CONCENTRATION - 20 SECOND EXPOSURE PERIOD.

CANMET 24ST. 23440-49293		
FIG: 13	19/07/85	

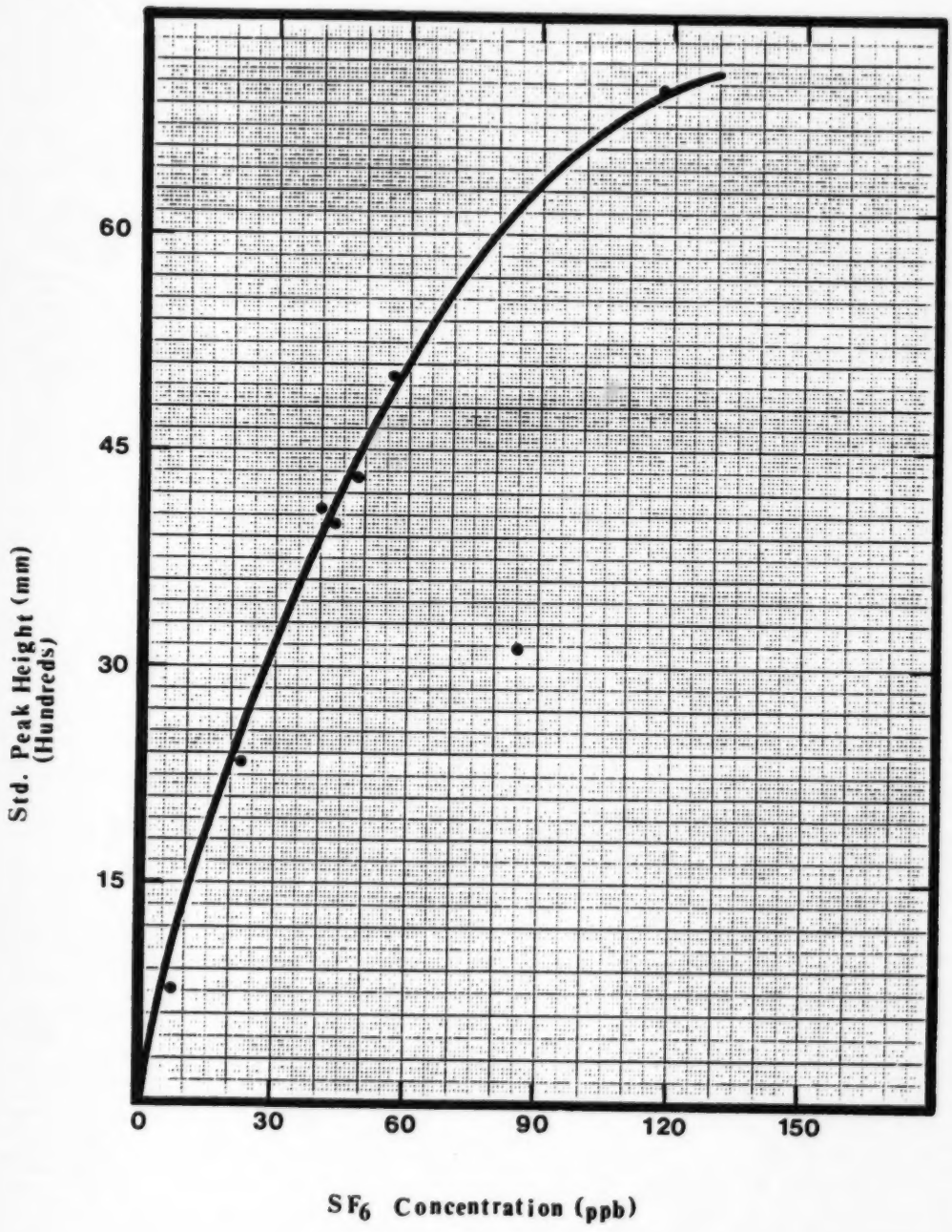


FIGURE 14: PEAK HEIGHT RECORDED AS A FUNCTION OF SF_6 CONCENTRATION - 30 SECOND EXPOSURE PERIOD.

CANMET 24ST. 23440-49293		
FIG: 14	19/07/85	

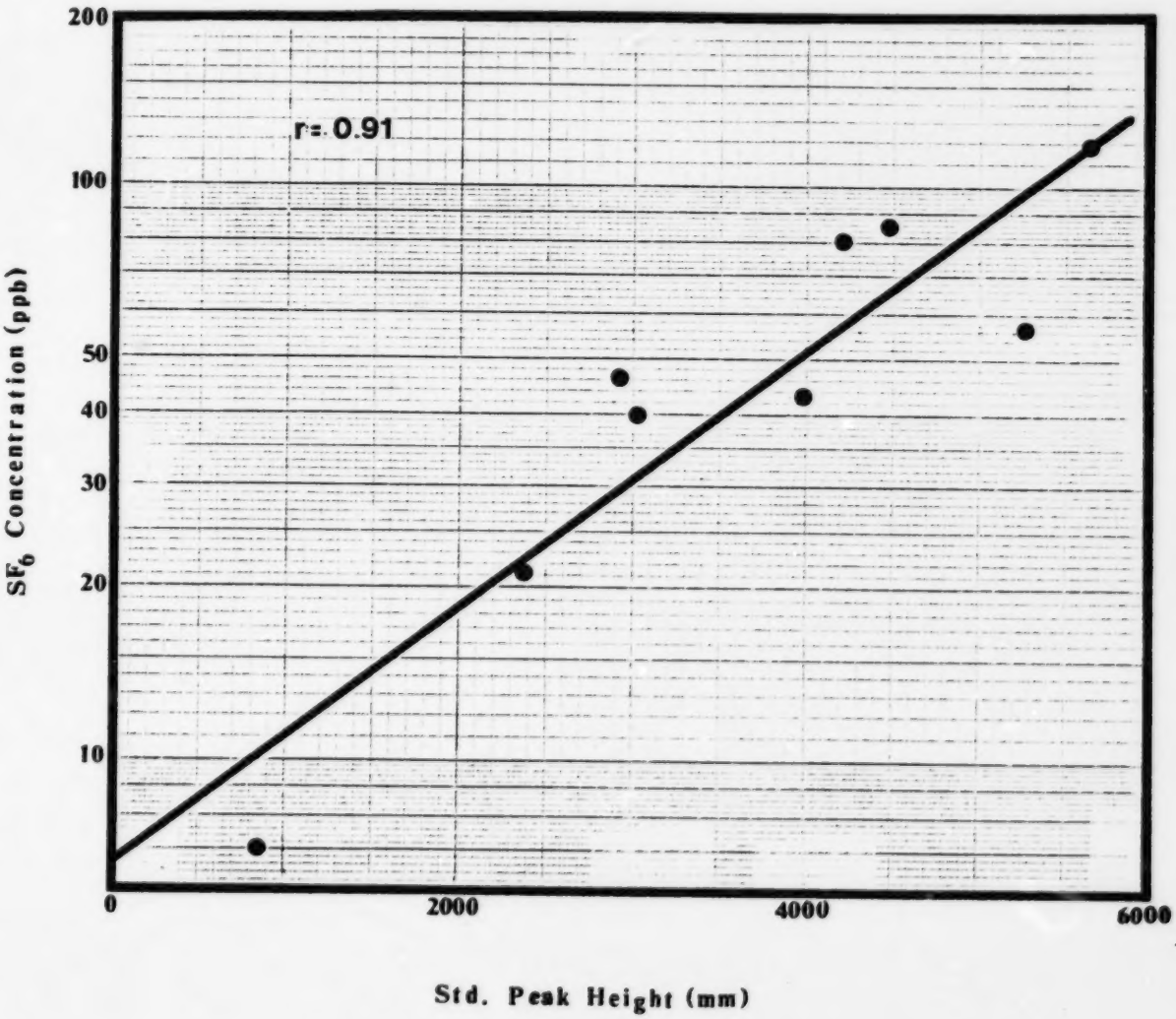


FIGURE 15: LOG SF_6 CONCENTRATION (ppb) AS A FUNCTION OF PEAK HEIGHT RECORDED (mm).

CANMET 24ST. 23440-49293		
FIG: 15	19/07/85	SK

variability in our results - variation in the size of the cloth sampler. This source of variation is readily apparent from Figure 16 which shows the results of exposure of different cloth samplers to SF_6 concentrations ranging from 0-120 ppb and Figure 17 which shows the isolated results obtained with one single cloth sampler. It is obvious that more stringent quality control will have to be exercised on the effective area of the sampling cloth during future tests if this important source of variations is to be minimized.

SF_6 Adsorptivity of CDE Charcoal Cloth Versus Activated Nutshell Charcoal

The relative quantities of SF_6 tracer gas collected passively on CDE charcoal cloth and on activated nutshell charcoal by active sampling are compared in Table III. As reported elsewhere (6), it is readily apparent from these results that charcoal cloth is an order of magnitude more efficient for collecting SF_6 than granulated charcoal.

CDE Charcoal Cloth Concomitant Exposure to SF_6 and Methane

During preliminary tests, CDE charcoal cloth (bare) samples were exposed to a mixture of 0.9% methane and 0.7 ppb SF_6 in the environmental chamber for various exposure periods (at ambient temperature and humidity) to assess the effect this gas would have on the cloth's SF_6 adsorptivity. The results, shown in Figure 18, indicated that the cloth apparently adsorbed 25% less SF_6 at this concentration than that obtained earlier. However, subsequent tests performed

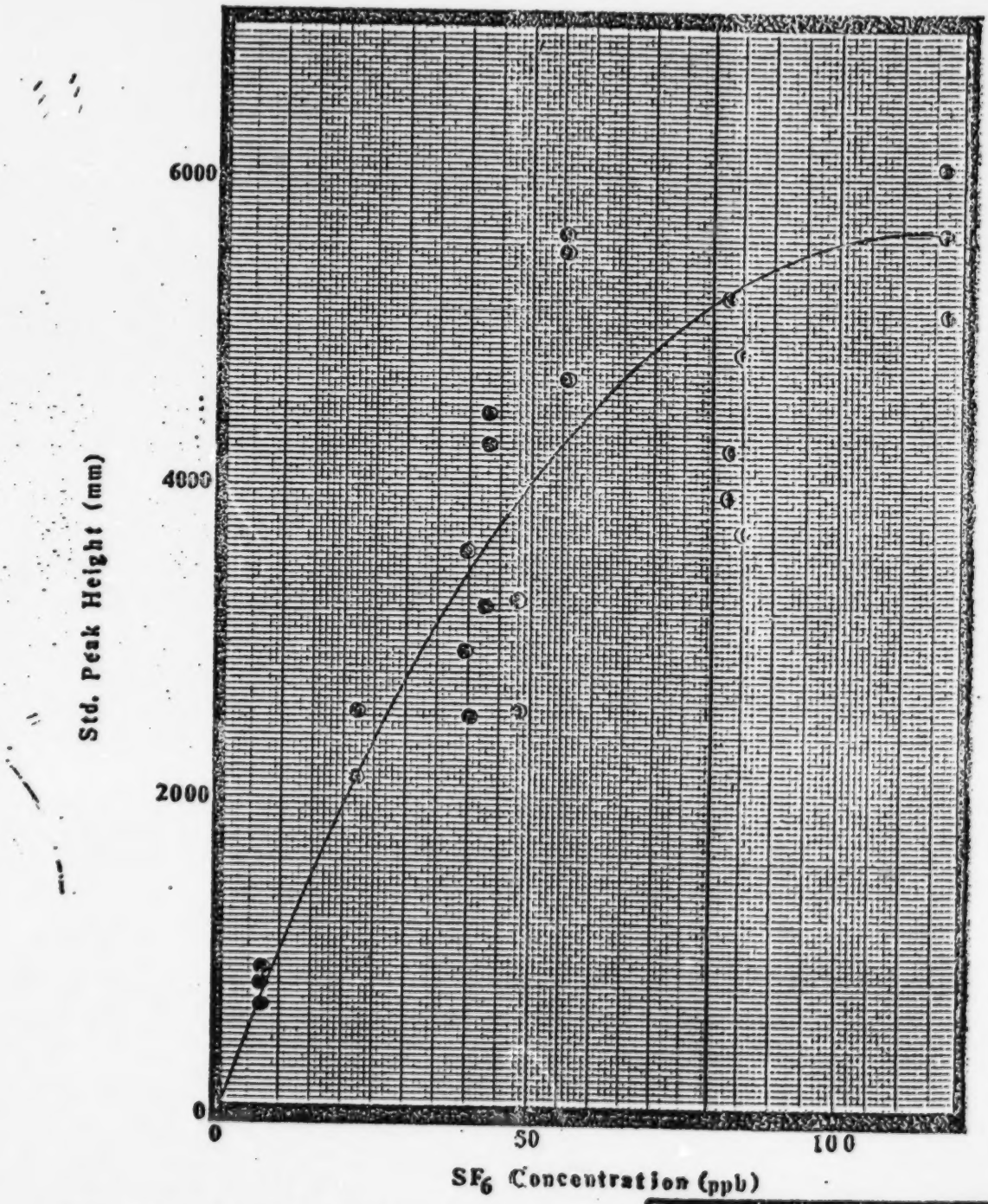


FIGURE 16: PEAK HEIGHTS RECORDED AFTER THE THERMAL DESORPTION OF VARIOUS BRASS MESH/ CLOTH SAMPLERS EXPOSED TO DIFFERENT CONCENTRATIONS OF SF_6 FOR 10 SECONDS.

CANMET 24ST. 23440-49293		
FIG:16	19/ 07/ 85	

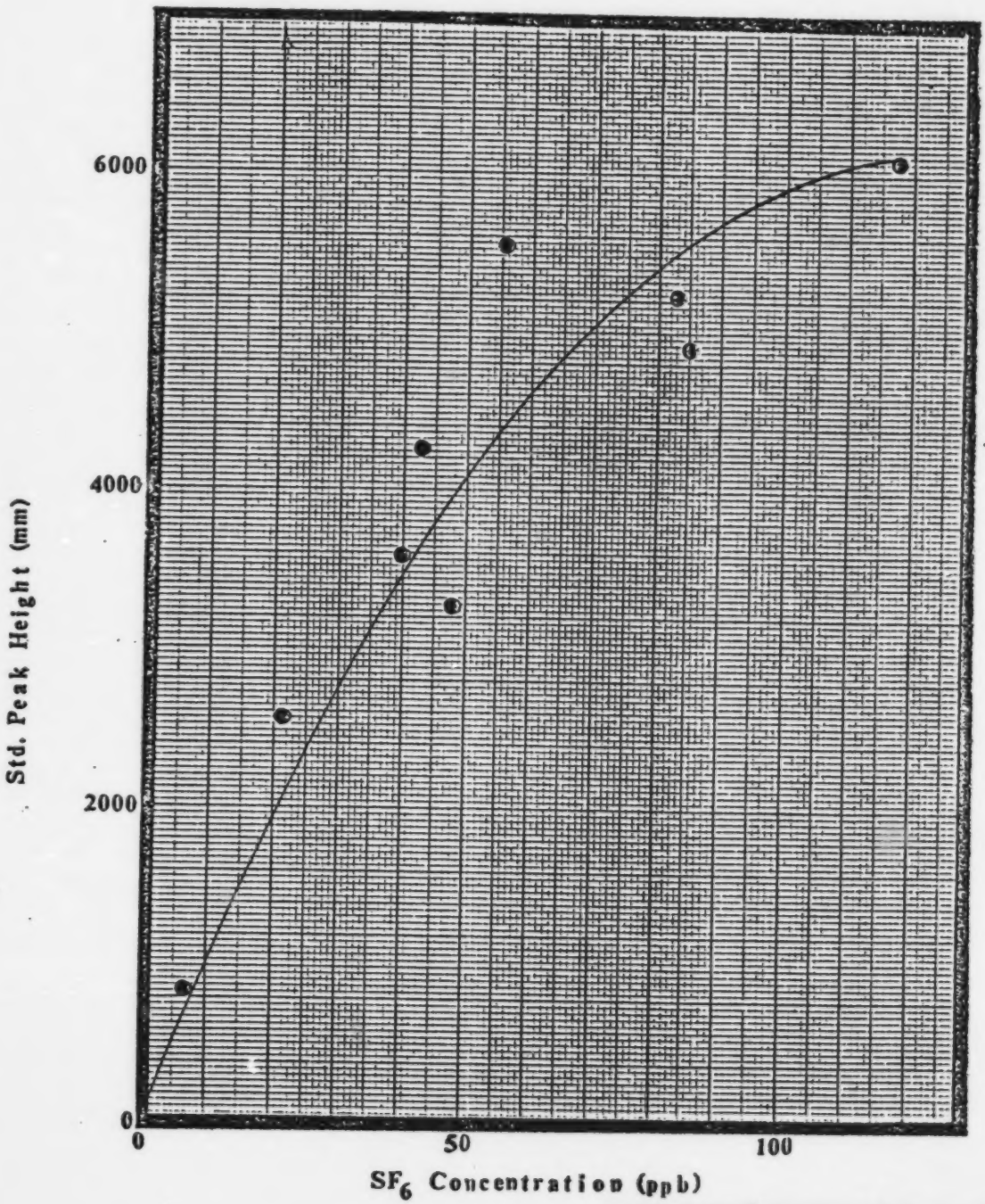


FIGURE 17: PEAK HEIGHTS RECORDED AFTER THERMAL DESORPTION OF A SINGLE BRASS MESH/CLOTH SAMPLER (#5) EXPOSED TO DIFFERENT CONCENTRATIONS OF SF_6 FOR 10 SECONDS

CANMET 24ST. 23440-49293		
FIG:17	19 / 07/ 85	

Table III. Comparison of the Relative Amounts of SF_6 Collected on Granulated Nutshell Charcoal and CDE Charcoal Cloth

Sample	Adsorbent Weight (mg)	SF_6 Concentration (ppb)	Sampling Rate (mL/second)	Sampling Time (seconds)	Amount of SF_6 Collected (ng)
Granulated Charcoal	500	3.5	0.21	10	0.045
	500	3.7	0.21	20	0.094
	500	3.7	0.21	30	0.141
	500	10.7	0.21	10	0.27
	500	10.7	0.21	10	0.27
CDE Charcoal Cloth	50	22.9	unknown	10	0.47
	50	22.9	unknown	10	0.47
	50	22.9	unknown	10	0.47

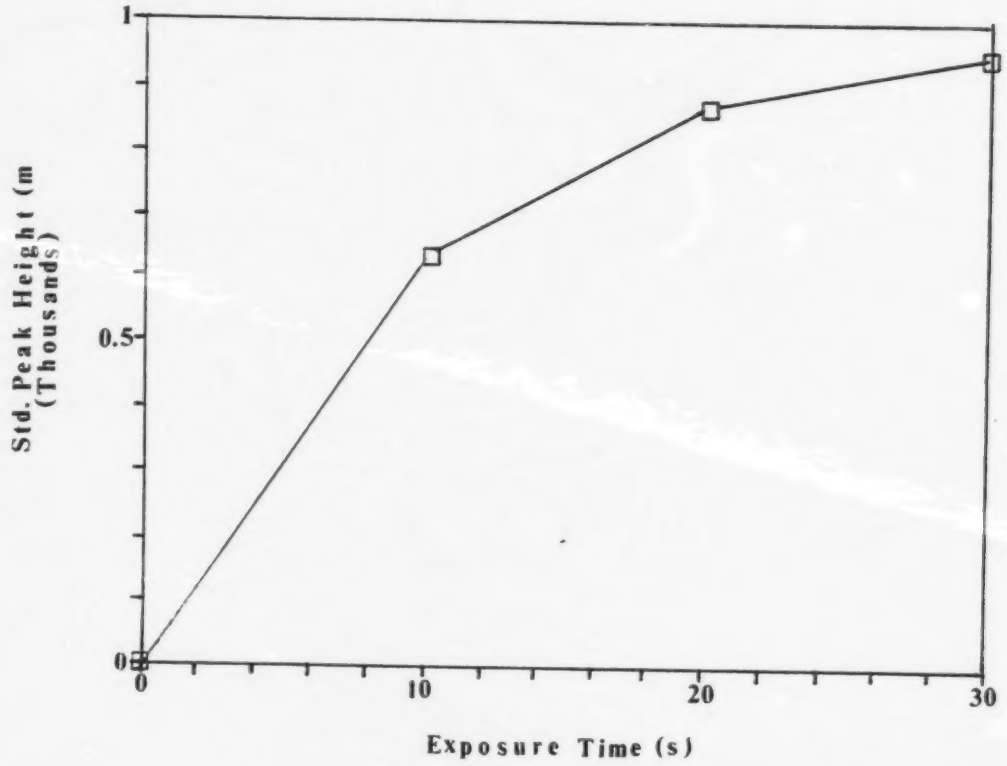


FIGURE 18: EFFECT OF 0.9% METHANE IN AIR ON CDE CHARCOAL CLOTH'S CAPACITY TO ADSORB SF_6 (0.7 ppb) OVER VARIOUS EXPOSURE TIMES.

CANMET 24ST. 23440-49293		
FIG:18	19 /07/ 85	

at 1.0 and 1.3 ppb SF_6 and 0.9% methane showed a minimal effect. These exposure tests were repeated with the brass mesh/cloth samplers and the results of one such test performed with a single tube (to minimize the inter-tube variability discussed earlier) at various methane concentrations ranging from 3.0 to 5.0% and at an exposure time of 10 seconds are shown in Figure 19. According to these and other results, methane concentrations at levels exceeding those normally found in a coal mine, has but a minimal effect on the cloth's adsorptivity of SF_6 at tracer gas concentrations ranging from 0 to 50 ppb. Unfortunately, we experienced difficulties in generating higher concentrations ranging from 0 to 50 ppb. Unfortunately, we experienced difficulties in generating higher concentrations of tracer gas in the presence of methane gas in the 3-5% range. Further tests are being conducted and these will be reported separately. In view of the results obtained to date, it is anticipated that methane gas concentrations at the levels used for these tests will have a minimal effect on the cloth's capacity to adsorb SF_6 at higher concentrations.

Effect of Humidity on the Adsorption Capacity of CDE Charcoal Cloth

Prior to conducting tests to assess the effects of humidity levels likely to be found in coal mines on the capacity of charcoal cloth to adsorb SF_6, we acquired a new gas chromatograph equipped with an electron capture detector

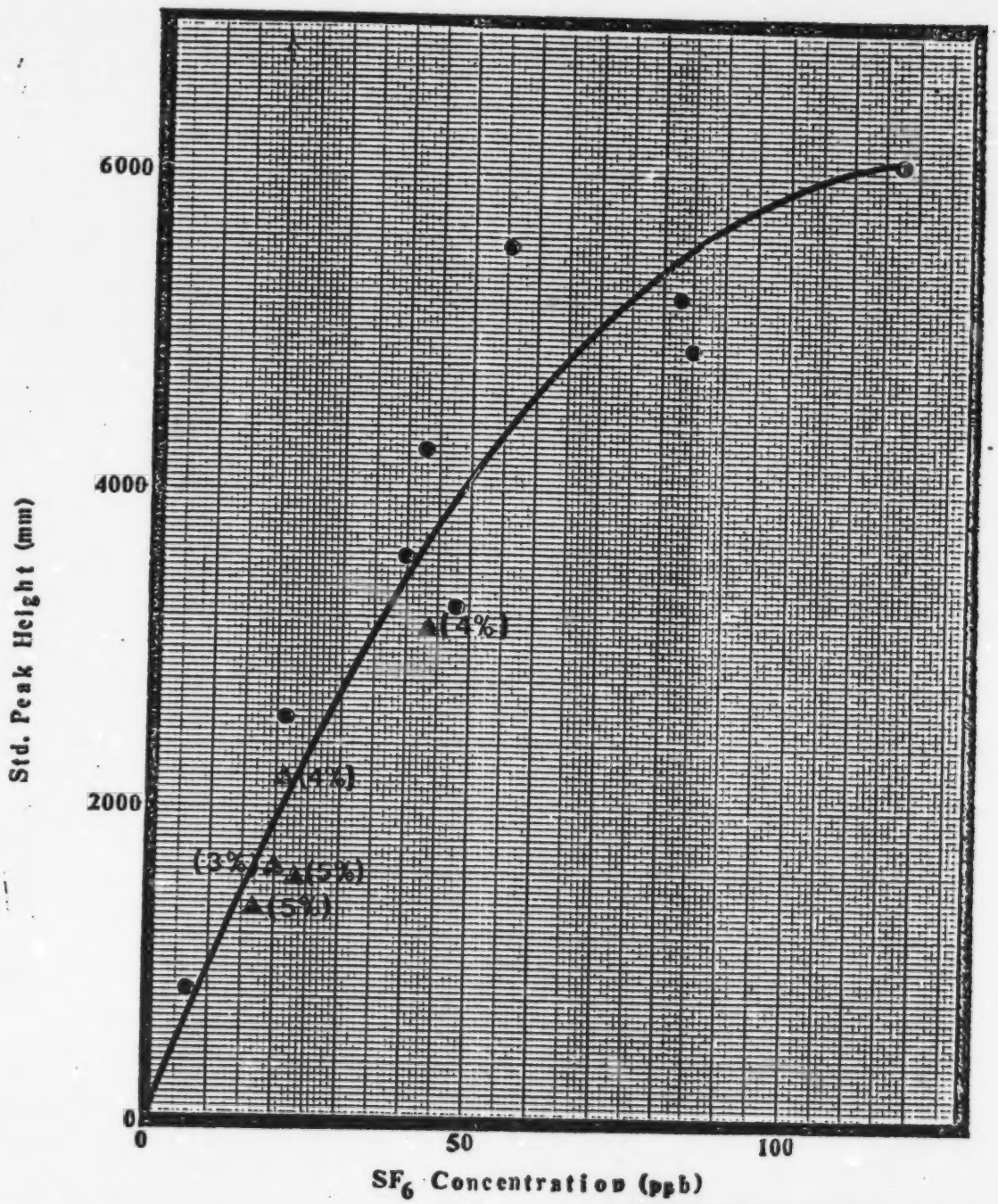


FIGURE 19: COMPARISON OF PEAK HEIGHT RECORDED AFTER THE THERMAL DESORPTION OF BRASS MESH/CLOTH SAMPLER EXPOSED TO VARIOUS CONCENTRATIONS OF SF_6 IN THE ABSENCE (●) AND PRESENCE OF DIFFERENT CONCENTRATIONS OF METHANE GAS (▲)

CANMET 24ST. 23440-49293		
FIG:19	19 / 07 / 85	

(Perkin-Elmer model 8037B) which was to be dedicated to the Perkin-Elmer ATD-50 thermal desorber. This necessitated a three-week shutdown in our operations to interface the two instruments, to allow staff members time to familiarize themselves with the new configurations and to calibrate the new detector's response. On resumption of the tests to assess the effect of humidity we discovered that the electron capture detector in the new instrument was almost an order of magnitude more sensitive to SF_6 and the dynamic range had been shifted to lower SF_6 concentrations. In fact, the electron capture detector became saturated during the analysis of the SF_6 thermally desorbed from test samplers exposed to <20 ppb SF_6 for 10 seconds! All attempts to date to remedy this instrumental problem have been futile. As a result, the test results reported here involve test cloth exposures to SF_6 concentrations < 20 ppb. It is anticipated that these concentrations < 20 ppb. It is anticipated that these instrumental problems are not insurmountable, and results obtained with these tests at higher SF_6 concentrations will be reported later.

The results obtained by exposing the brass mesh/cloth samplers to 15 and 7 ppb concentrations of SF_6 at 92% relative humidity are shown in Figures 20 and 21 respectively. The results are compared to those obtained at ambient humidity on that day. It should be noted that the differences in humidity on the test (19 and 37% respectively) are not the same for both tests and may have a considerable

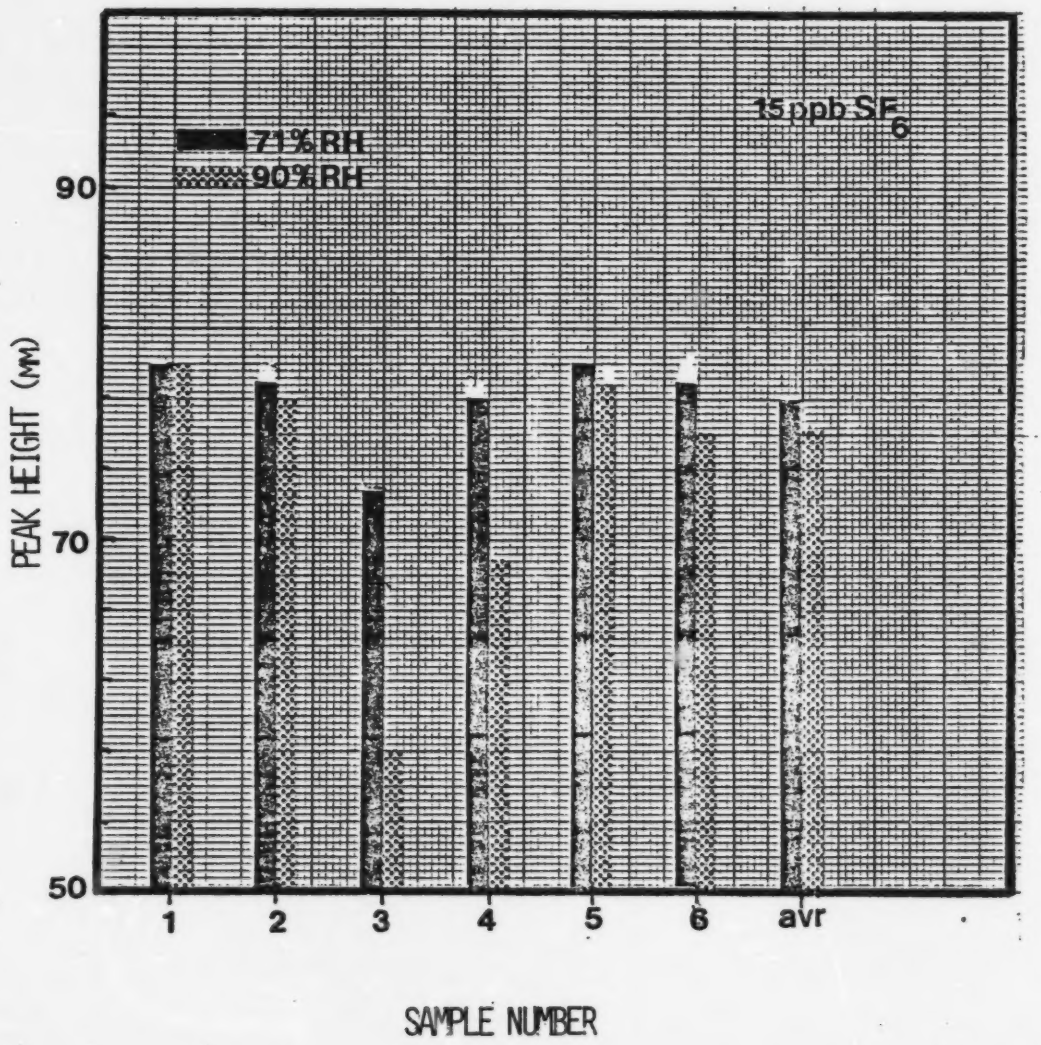


FIGURE 20: EFFECT OF HUMIDITY ON THE ADSORPTIVITY OF CDE CHARCOAL CLOTH (SF_6 - 15 ppb) SAMPLING PERIOD 10 SECONDS

CANMET 24ST. 23440-49293		
FIG:20	19/07/85	

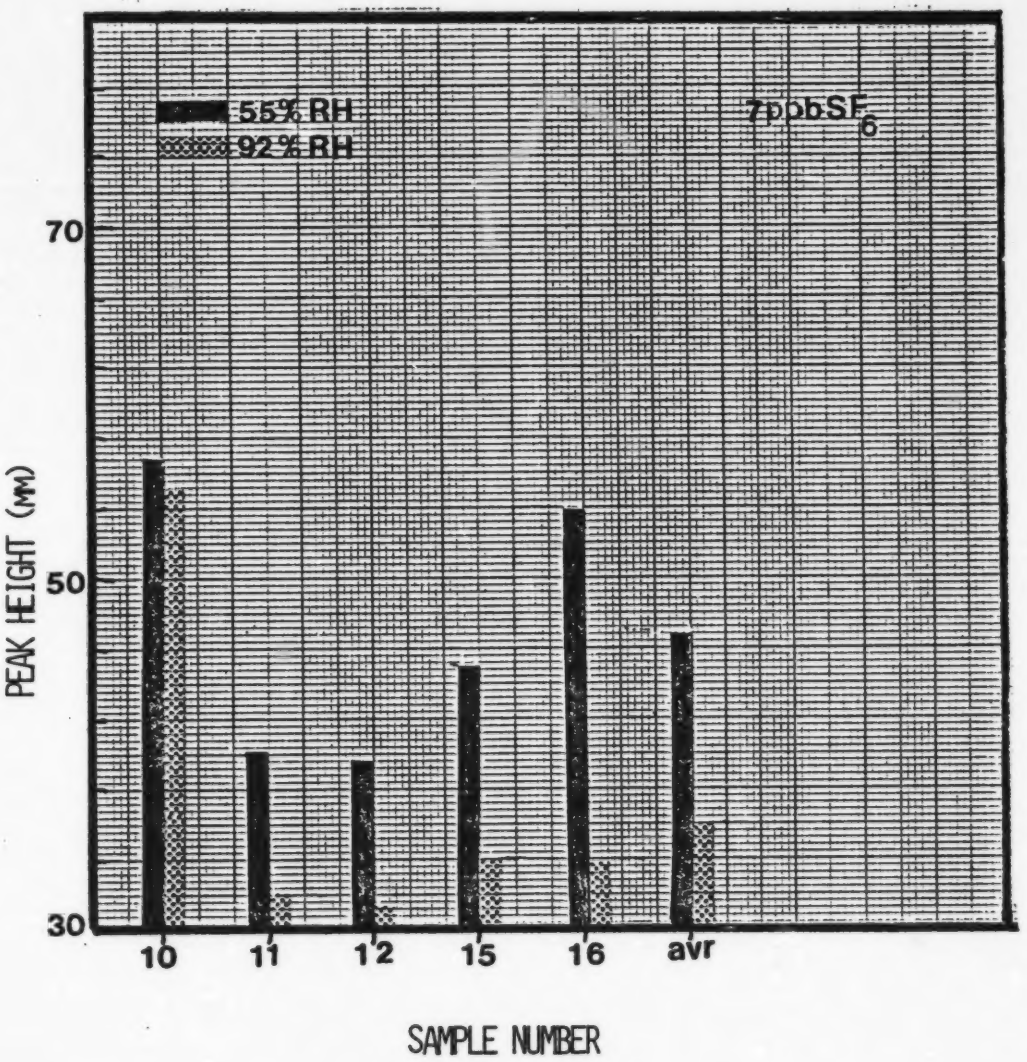


FIGURE 21: EFFECT OF HUMIDITY ON THE ADSORPTIVITY OF CDE CHARCOAL CLOTH (7 ppb SF_6, 10 SECOND SAMPLING PERIOD)

CANMET 24ST. 23440-49293		
FIG:21	19/07/85	

bearing on the results obtained. Thus, the results shown in Figure 20 indicate that a change of relative humidity from 71 to 90% caused a significant but not inordinate change in the cloth's adsorptivity for SF_6 at 15 ppb. However, a change of relative humidity from 55 to 92% had a marked effect on the cloth's capacity to adsorb SF_6 at a 7 ppb concentration. The difference in results could be attributed to the two-fold difference in the change in relative humidity. Conversely, it is possible that relative humidity may have a more significant effect on the cloth's absorptivity at relatively low SF_6 concentrations.

This effect of relative humidity on the ability of charcoal to adsorb a gas such as SF_6 is not unexpected. The converse would be true. The marked reduction of the capacity of charcoal cloth to adsorb certain organic vapours at high relative humidity has been reported elsewhere [6]. We do not believe that this will be a limitation on the applicability of the cloth to sample SF_6 in a mine environment where, it is assumed, humidity conditions are relatively constant and the sum total effect would be to reduce somewhat the amount of SF_6 taken up by the cloth.

Ambient Effect of Methane Gas and Humidity on the SF_6 Adsorptivity of CDE Charcoal Cloth

For the reasons stated earlier we have not been able to conduct satisfactory tests for the combined effects of methane gas and humidity on the adsorption capacity of CDE

charcoal cloth. However, preliminary tests conducted at relatively low SF_6 concentrations, 1.0 and 1.3 ppb, and 0.9% methane gas have indicated that their combined effects should not differ greatly from their individual influence on the cloth's absorptivity (Table IV). That is, methane's effect

Table IV. Combined Effect of Relative Humidity and 0.9% Methane in Air Concentration on CDE Charcoal Cloth's Ability to Adsorb SF_6 Gas

Exposure Time (seconds)	SF_6 Conc. (ppb)	Methane Gas Conc. (%)	R.H. (%)	SF_6 Peak* Height Obtained (mm)	Previous SF_6 Peak Height Obtained (mm)
10	1.0	0.9	87	1200 ± 346	1200
10	1.3	0.9	78	1572 ± 91	1450

* Corrected to an attenuation of 16.

up to a 5% concentration will be negligible while humidity will have a significant effect. It is therefore anticipated that their combined effect will not differ significantly from that obtained with humidity alone. We expect to be in a position to prove this experimentally soon.

Effects of Barometric Pressure on the Adsorptive Capacity of CDE Charcoal Cloth

It has been shown [15] that the diffusion coefficient

for a gas such as SF_6 would decrease by some 14% with a rise of barometric pressure from 94.6 to 107.9 kPa. However, at the same time, such a change in barometric pressure would also affect the concentration of the gas in that the concentration is itself directly proportional to pressure. As a result, the total mass collected by the cloth is independent of pressure [16]. Hence, there would be no purpose to experimentally verify the effect of increases in barometric pressure on the cloth's capacity to adsorb SF_6.

Sample Integrity

Exposure of paired sets of charcoal cloth to known concentrations of SF_6 for 10, 20, and 30 seconds and the thermal desorption of paired samples 24 hours apart showed no loss of adsorbed gas during storage. Hence, it would appear that exposed cloth samples can be safely stored for periods up to 24 hours without significant loss of collected gas.

CONCLUSIONS

Tests conducted to date have shown that CDE charcoal cloth has the capacity to adsorb SF_6, in 10 seconds or less, from environments having levels of the tracer gas ranging to 120 ppb. The cloth also allows the accurate analysis of the gas by a gas chromatograph equipped with an electron capture detector, up to 24 hours after its collection.

Sampling periods greater than 20 seconds are not recommended at this time since factors which may include an isokinetic effect, markedly affect the results obtained. Variable results obtained at sampling periods <10 seconds are mainly due to experimental error and, more precisely, a timing error over which we have no control. Therefore, all future tests will be conducted at exposure time intervals ranging from 10 to 20 seconds. It is anticipated that further modifications of the test sampler such as increasing the path of diffusion (L) will allow us to sample for longer periods of time and will lessen the effects of parameters such as the isokinetic effect. It is evident that the use of brass mesh to cover the cloth samples has had but a minimal effect on these parameters.

Under present experimental conditions, the amount of SF_6 adsorbed by the charcoal cloth varies as the logarithm of the atmospheric concentration of SF_6. The saturation point for the cloth has not been estimated. However, present data and the results reported by others lead us to believe that

this concentration will be in excess of 120 ppb.

An important source of variation of the results has been identified as differences in the effective area of the cloth. This would indicate that great care and a certain degree of quality control will be required in the preparation of the charcoal cloth samplers if reproducible results are desired.

As reported elsewhere, CDE charcoal cloth's capacity to adsorb SF_6 has been shown to be at least an order of magnitude better than that of granulated nutshell charcoal.

Tests performed to date have conclusively shown that atmospheric concentrations of methane gas ranging to 5% have a minimal effect on the adsorption of SF_6 by charcoal cloth from atmospheres of tracer gas ranging to 50 ppb. Experimental problems have prevented us from testing this potential effect at higher SF_6 concentrations. However, it is anticipated that this effect, if it exists, will be minimal at methane concentrations found in coal mines and for cloth exposure times <10 seconds.

Instrumental problems have limited the tests we have been able to conduct on the effect of humidity on the adsorptive capacity for SF_6. Nonetheless, the results obtained for SF_6 concentrations of 7 and 15 ppb do indicate that marked changes in humidity will significantly reduce the capacity of the charcoal cloth to adsorb the gas. It is

expected that this effect will also exist at higher concentrations of SF_6. Nevertheless, the cloth's capacity to adsorb SF_6 will not be inordinately impaired at relative humidity >90% for sampling times of 10 seconds or less. If it is further assumed that humidity conditions in a coal mine are relatively stable, we do not believe that this parameter will present a serious impediment to the use of CDE charcoal cloth as the basis for a sequential tracer gas sampler for coal mine environments.

Only preliminary tests have been performed on the combined effects of humidity and methane gas. Nonetheless, it is anticipated that this effect will not differ markedly from that of humidity alone.

Our recent experience has demonstrated that care must also be exercised in the choice of a gas chromatograph to perform the analysis of SF_6 thermally desorbed from charcoal cloth. These instruments' detectors differ as to the sensitivity and linear dynamic range of their electron capture detector. A wrong choice could seriously jeopardize the analysis of collected samples if the detector is easily saturated at relatively low concentrations.

RECOMMENDATIONS

1. Tests should be conducted at high SF_6 concentrations (>20 ppb) to further assess the impact of high humidity on the adsorptivity of CDE charcoal cloth for short sampling periods.

2. Tests should be conducted at high SF_6 concentrations (50-150 ppb) to confirm the lack of effect of methane (levels < 5%) on the adsorptivity of CDE charcoal cloth for short sampling periods.

3. CDE charcoal cloth should be exposed jointly to methane gas and elevated humidity to determine their combined effect on the cloth's capacity to adsorb SF_6 for short sampling periods.

4. To ensure constancy of the cloth sampler's effective area, they could be prepared by a technique used in the textile manufacturing sector and this area verified by quality control tests to determine their suitability.

5. A series of tests could be conducted on various configurations of CDE charcoal cloth samplers to assess their performance under actual mine conditions. This would assist us in determining optimal design parameters including the diffusion path (L) and the cloth's effective exposure area (A) and sampling time (t).

REFERENCES

1. Bailey, A. and Maggs, F.A.P., Fibrous Carbon - British Patent 1301101 (1972) 7 pp.

2. Maggs, F.A.P., Capon, A., and Smith, M.E., Activation of Fibrous Chars, Ext. Abst. Program - Biennial Conference, Carbon 13: 386-7 (1977).

3. Maggs, F.A.P., Robins, G.A., and Smith, M.E., Physical Properties of CDE Charcoal Cloth, Ext. Abst. Program - Biennial Conference, Carbon 13: 441-442 (1977).

4. Maggs, F.A.P., Robins, G.A., and Smith, M.E., Adsorptive Properties of CDE Charcoal Cloth, Biennial Conference, Carbon 13: 3-4 (1977).

5. Bailey, A. and Smith, M.E., The Adsorption of Low Boiling Gases by Activated Charcoal Cloth, Est. Abst. Program - Biennial Conference, Carbon 17: 232-233 (1981).

6. Smith, M.E. and Davies, J.A., Comparison of the Adsorptive Performance of CDE Charcoal Cloth and Granular Charcoal, Biennial Abst Program, Carbon 19:323-324 (1983).

7. Maggs, F.A.P. and Robins, G.A., Symposium on Characterization of Porous Solids Neuchatel, July (1978).

8. Technical Notes, Charcoal Cloth Limited, Maidenhead, Berkshire, England.

9. Bailey, A. and Hollingsdale-Smith, P.A., A Personal Diffusion Sampler for Evaluating Time-Weighted Exposure to Organic Vapours and Gases, Ann. Occup. Hygiene 30:345-356 (1977).

10. Koresh, J. and Soffer, A., J. Chem. Soc. Faraday Transactions 76 (2), pp.2457-71 (1980).

11. Koresh, J. and Soffer, A., J. Chem. Soc. Faraday Transactions 77 (12) pp.3005-3018 (1981).

12. Barton, S.S. and Koresh,J., J. Chem. Soc. Faraday Transactions 78, pp. 1147-1154 (1982).

13. Barton, S.S. and Koresh, J., J. Chem. Soc. Faraday Transactions 79 (5), pp. 1157-1164 (1983).

14. Barton, S.S. and Koresh, J., J. Chem. Soc. Faraday Transactions 79 (5), pp. 1164-1174 (1983).

15. Tompkins, F.C. and R.L. Goldsmith, A New Personal Dosimeter for Monitoring of Industrial Pollutants, Am. Ind. Hyg. Assoc. J. 38: 371-377 (1977).

16. Rose, Vernon E. and Perkins, Jimmy L., Passive Dosimetry - State of the Art Review, Am. Ind. Hyg. Assoc. J. 43 (8): 605-621 (1982).